UNIVERSITY OF VIRGINIA
SCHOOL OF CHEMISTRY

KINETICS OF TRANSITIONS IN POLYMORPHIC SOLIDS

By
RAYMOND D. COOL

Extract from a dissertation presented to the Graduate Faculty of the University of Virginia in candidacy for the degree of Doctor of Philosophy

MAY, 1928

L. C.

3781
V81C
UNCLASSED
Dissertation

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

UNIVERSITY OF VIRGINIA
SCHOOL OF CHEMISTRY

KINETICS OF TRANSITIONS IN POLYMORPHIC SOLIDS

By
RAYMOND D. COOL

Extract from a dissertation presented to the Graduate Faculty
of the University of Virginia in candidacy for the
degree of Doctor of Philosophy

MAY, 1928

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the advice received from Professor Arthur F. Benton, who suggested and directed this investigation.

KINETICS OF TRANSITIONS IN POLYMORPHIC SOLIDS

BY RAYMOND D. COOL

Introduction

It is well known that in chemical changes in which at least one of the reactants and one of the products is a solid phase, the reaction is commonly autocatalytic. After a longer or shorter period of "incubation," the rate increases (induction period), reaches a maximum and then decreases, finally falling off to zero when the reaction is complete. The phenomenon is interpreted on the assumption that reaction proceeds more readily at the interface between the two solid phases than elsewhere, and that the rate of reaction is proportional to the extent of this interface. The only necessary condition for the appearance of this type of autocatalysis appears to be the occurrence of a separate solid phase on each side of the reaction equation. It has been observed[1] in reactions in which one solid produces a second solid and a gas (decomposition of Ag_2O, $AgMnO_4$, $Ag_2C_2O_4$, various metallic carbonates, etc.), and in those in which a solid and a gas react to form a second solid and a gas (reduction of CuO, NiO, Ag_2O, etc., by hydrogen or carbon monoxide); it is occasionally observed in reactions in which a solid and a gas react to form a second solid (hydration of salts, oxidation of metals at low temperatures, etc.).

In addition to these three, a fourth type of reaction is available for study, namely, those in which all the participants are in the solid state. An example is the transition of a polymorphic solid, involving nothing but one solid reactant and one solid product. It appears that this case might be less complex, especially from the theoretical stand-point, than any of the other three cases cited.

Observations of allotropic transformations have indicated that in certain cases at least, reaction proceeds more readily at the boundary between the two solid phases than elsewhere.[2] It appears, however, that little attention has been given to the kinetics of allotropic changes as a function of the quantity of material transformed. Estimates of the velocity of transformation have been obtained dilatometrically in a few cases, but the assumption is usually implied that at a given temperature the rate is independent of the extent to which reaction has proceeded. Furthermore, in these experiments the solid under study was always in contact with the dilatometer liquid, which through solubility or adsorption effects might have considerable influence on the rate of reaction. In certain cases a marked effect has been observed.[3]

---

[1] For a discussion of the results obtained in this field, see Taylor: "Treatise on Physical Chemistry," 2nd Ed., **2**, pp. 1067-9.

[2] See, for example, Cohen and coworkers: Z. physik. Chem., **30**, 601 (1899), **63**, 625 (1908); Bridgman: Proc. Am. Acad. Arts Sci., **52**, 57 (1916); Early and Lowry: J. Chem. Soc., **115**, 1387 (1919).

[3] Cohen: Z. physik. Chem., **14**, 53; Cohen and Bredig: 535 (1894).

In view of these facts it was decided to study the kinetics of certain allotropic transformations by employing a dilatometer in which the volume changes are transmitted by means of an inert gas rather than by a liquid.

Experimental Method

Apparatus.—The dilatometer consisted of a glass bulb sealed at the top to a capillary tube leading to a 3-way stopcock, one arm of which was open to the atmosphere, and the other was connected to a closed vacuum manometer of 2 mm. glass capillary. The adjustment of the mercury levels in the manometer was effected by means of a mercury well and glass plunger so that the redistilled mercury was never in contact with rubber. The manometer levels were read with the help of a wood scale sliding in brass guides and counterbalanced so as to remain in any desired position. The scale carried two pointers, exactly 760.0 mm. apart, which were illuminated by small electric lights mounted on the scale. Two small mirrors, set at an angle of 45°, were also attached to the scale, one at the level of each pointer. By this device the image of the upper mercury level and pointer was brought down to the lower mirror and there reflected to the eye at the height of the lower level and pointer, thus facilitating simultaneous reading of the two levels. This somewhat complicated manometer was resorted to only after preliminary experiments with an open manometer had shown that even small fluctuations in barometric pressure were sufficient to vitiate the results.

Careful temperature control is also essential if reliable results are to be obtained. To this end, the bulb was surrounded by an electrically heated vapor bath, jacketed with asbestos paper, and tightly closed at the top with a cork stopper cemented with litharge-glycerine cement. This stopper carried a calibrated thermometer graduated to 0.1°, a narrow capillary tube by means of which air could be bubbled through the bath liquid, when necessary, to prevent bumping, and a reflux condenser. The latter was in turn connected to a 3-way stopcock so that the vapor bath could be opened to the air, or connected to a device for maintaining a constant pressure. The pressure regulator was similar to the one described by Scofield.[1]

Procedure.—A liquid whose boiling point was above the transition temperature was used in the vapor bath. For transitions from the high temperature form to the low temperature form, the bath was at first closed off from the pressure regulator, and run at atmospheric pressure to convert the sample into the high temperature form. After a suitable time the bath was connected to the regulator, in which in the meantime the pressure had been adjusted to give the temperature at which the measurement was to be made. As soon as this temperature was approximately attained, the sample, which had previously been open to the air through a calcium chloride tube, was connected to the manometer. With the mercury levels kept 760 mm. apart to insure constancy of pressure in the bulb, the rate of reaction was followed by reading the height of the mercury column in the calibrated arm of the manometer

[1] Schofield: Ind. Eng. Chem., **18**, 717 (1926).

at five-minute intervals. For transitions from the low temperature form to the high, the procedure was the same, except that the preliminary heating with the bath at atmospheric pressure was not required.

Materials.—The experiments to be reported here deal with the transitions of mercuric and of thallous iodides. These substances were chosen because their transitions occur at convenient temperatures and are accompanied, in both cases, by pronounced color changes. Samples 1-3 of mercuric iodide were used only in preliminary experiments, and their preparation need not be described. Samples 4 and 5 were made from recrystallized mercuric chloride and potassium iodide according to the procedure given in U.S. Pharmacopoeia, 8th Revision, p. 237. Sample 4 was also recrystallized from alcohol, and both samples were dried for about 100 hours in an oven at 110°.

Thallous iodide was prepared from C. P. potassium iodide and thallous nitrate. The resulting precipitate was carefully washed and dried before use.

The liquids used as vapor baths were not especially purified. Those most largely employed were water, amyl alcohol, aniline, xylene, acetic acid and benzaldehyde.

Results

Reliability of the Method.—At different times a number of trials were made to determine how closely manometer readings could be checked by displacing the mercury columns and then restoring them to a difference of 760 mm. In these trials readings could be regularly reproduced within 1 mm., and consequently in following reaction rates the manometer was read to this degree of precision only.

Table I indicates the extent to which the rate of reaction is reproducible in experiments carried out under identical conditions. In each of these runs the sample (No. 4) was first heated for one hour at 137° to convert it into the yellow form, and the rate of transition to the red form measured at 120.2°. It should be mentioned, however, that the reproducibility was by no means always so satisfactory as in Runs 31-4, owing to slight fluctuations in the temperature of the vapor bath. Fortunately, this difficulty was serious only when water or benzaldehyde was used as bath liquid.

TABLE I

Reproducibility of Rate Measurements

Run	Time to reach max. rate (min.)	Rate at max. (cm/5 min.)	Time for complete reaction (min.)	Total reaction (cm.)
31	35	1.0	75	7.4
32	35	1.1	75	7.7
33	35	1.2	65	7.9
34	35	1.1	75	7.8

In order to secure reliable information regarding the early stages of reaction, careful studies were made to determine the time required for temperature equilibrium to be established throughout the sample after the temperature of the bath had been suddenly changed. This was accomplished by

observation of the manometer when the temperature was changed to the same extent as in a regular run, but without passing through the transition temperature, and also, in some cases, by comparison of the readings of the thermometer in the vapor bath with a second thermometer inserted in a well at the center of the sample. It was found that equalization of temperature required 15 min. for mercuric iodide, Sample 4 (bulb 13 cm. long and 1.8 cm. in inside diameter), 5 min. for mercuric iodide, Sample 5 (bulb 132 cm. long and 0.5 cm. in diameter, wound in a spiral), 10 min. for thallous iodide, Sample 1 (bulb 1.5 cm. in diameter), and 10 min. for thallous iodide, Sample 2 (bulb consisting of three branches, each 12 cm. long and 1.5 cm. in internal diameter).

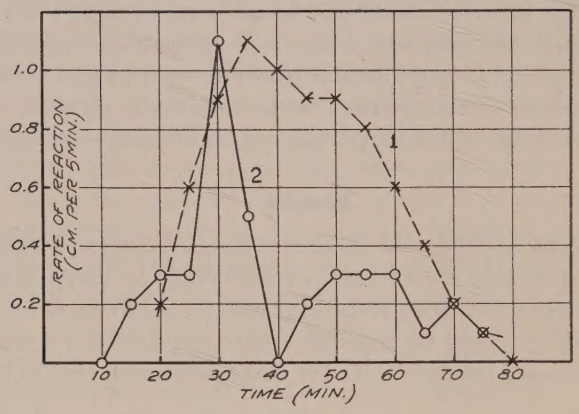

FIG. 1

Rate of transition of mercuric iodide.
Curve 1: Sample 4, yellow to red at 120.2°;
Curve 2: Sample 5, red to yellow at 130.0°.

Autocatalytic Nature of the Reactions.—Typical data from runs made under the best conditions are plotted in Figs. 1 and 2. Fig. 1 shows the rates of transition of mercuric iodide in both directions; Curve 1 represents the change, yellow to red, for Sample 4 (76.50 g.) at 120.2°, and Curve 2 represents the change, red to yellow, for Sample 5 (67.85 g.) at 130.0°. In Fig. 2 similar data are shown for thallous iodide; Curve 1 is the change, red to yellow, for Sample 1 (48.21 g.) at 142.0°, and Curve 2 is the change, yellow to red, for Sample 2 (107.61 g.) at 180.5°. On each curve the initial plotted point represents the first reading unaffected by temperature lag.

It will be seen that these transformations are autocatalytic in nature, and give curves of the same type as those for other systems involving two separate solid phases. The rate increased rather rapidly to a maximum and then fell off much less abruptly, so that only about 20-30% of the total change had occurred when the maximum rate was reached. This behavior ordinarily indicates that the reaction started and spread from a comparatively large number of centers. That this was the case was evident from visual observation of the colors of the samples as reaction proceeded. The process was never observed to start in only one or two places and spread from these, but spots

of the stable form appeared throughout and then continued to grow in size, finally merging into one another. In line with these observations also is the fact that the period of "incubation" was usually very short or entirely absent, except when the subsequent rate was very slow.

Rate of Reaction and Temperature.—The rate of reaction was found to increase with increasing distance from the transition temperature, both above and below. The relative rates are indicated in three ways: (1) time required for rate to reach the maximum, (2) the rate of change at the maximum, and (3) time required for completion of the total change. Table II contains typical data for the yellow → red transition of mercuric iodide (Sample 4), where the preliminary treatment of the sample was approximately the same in each case. (The transition temperature is near 127°).

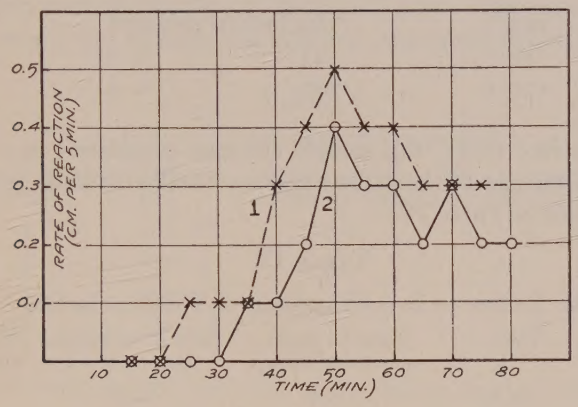

FIG. 2

Rate of transition of thallous iodide, Sample 1
Curve 1: red to yellow at 142.0°;
Curve 2: yellow to red at 176.0°

TABLE II

Yellow to Red Transition of Mercuric Iodide.

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min.)
23	98.5	<15	>8.0	25
24	116.0	45	1.0	85
30	120.2	55	0.9	105

Although changes at temperatures far removed from the transition temperature were too rapid for quantitative study, they could be followed qualitatively by observing the color change. The yellow form (Sample 1), on cooling to 50°, changed completely to red in less than 15 minutes. On cooling the yellow form (Sample 3) from 137° to 20°, it became completely red in less than 10 minutes, and a similar result was obtained on cooling it from 180° to 20°. At 122.8° this sample was less than one-third converted to the red form in 2.5 hours.

For the conversion of mercuric iodide to the high temperature form, it was found that at 129.5° Sample 3 changed to yellow only very slightly in 10 hours; at 136.7° the change required 40 minutes for completion, while at 181° reaction was complete in 10 minutes.

For thallous iodide the effect of temperature over the corresponding range is even greater. Table III shows results obtained with Sample I for the change, red to yellow. The preliminary treatment was substantially the same in each case. (The transition temperature is probably between 160° and 170°).

TABLE III

The Red to Yellow Transition of Thallous Iodide

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min).	Time for total reaction (min.)
22	131.2	Too fast to measure		20
23	142.0	45	0.5	150
26	150.0	460	0.5	>790

On cooling from 180° to 25° this sample changed completely in 2 minutes.

Data for the change of the same sample of thallous iodide in the reverse direction are given in Table IV.

TABLE IV

The Yellow to Red Transition of Thallous Iodide

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min.)
11	174.0	125	0.2	>720
20	176.0	50	0.4	>145
18	177.8	25	1.0	65
15	180.2	15	2.0	25

A number of workers[1] have found that the velocity of certain transformations from the high to the low temperature form passes through a maximum as the temperature is lowered. We have obtained qualitative evidence that the same is true of the cases under consideration. Thus when samples of mercuric iodide, sealed in tubes approximately 3 × 120 mm., were converted into the yellow form by heating and then immersed in liquid air, the yellow color immediately faded to white, but no further change occurred in 70 minutes at this temperature. On then permitting the tubes to warm up in a bath of petroleum ether, the salt gradually acquired its normal yellow color at −160° to −140°, and at the same time specks of the red form began to appear at numerous points. On reaching this stage, one sample was again cooled in liquid air, with the result that the progress of the transformation was completely stopped, the yellow portions fading to white and the red parts to orange.

[1] Gernez: Compt. rend., **100**, 1343, 1382 (1885); Tammann: "Kristallisieren und Schmelzen," (1903); Cohen and coworkers: Z. physik. Chem., **30**, 601 (1899); **33**, 57 (1900); **35**, 588 (1900).

It is evident that the rate of conversion at $-191°$ is very small, if not zero, and that the rate must pass through a maximum somewhere between this temperature and 20°.

Effect of Preliminary Treatment.—The rates of reaction of all samples were found to increase with the number of transformations previously undergone. This increase was very marked during the first few runs with a given sample. Thus for Sample 5 of mercuric iodide, with all other factors constant, the maximum rate was five times as great in the sixth run, and seven times as great in the ninth run, as in the first. However, the activity changed less and less in successive experiments, and finally reached a constant value.

The rate of reaction was also affected by the time and temperature of heating previous to a given transformation, as may be seen from the data in Table V, which refer to Sample 4 of mercuric iodide. Previous to these experiments the sample had attained its constant maximum activity.

TABLE V

Effect of Preliminary Treatment

Run	Time of heating at 137°(hr.)	Temp. of run	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min)
28	14	120.6°	85	0.4	>205
29	1	120.6°	35	0.9	125
30	5	120.2°	55	0.9	105
31	1	120.2°	35	1.0	75

Since the conversion of the red form to the yellow at 137° required less than 30 minutes for completion, the retarding effect of heating at this temperature for times in excess of one hour may be ascribed to growth of the crystals and gradual elimination of their imperfections, a process which would be facilitated by the appreciable volatility of the material. We have obtained no evidence either for or against the applicability of Smits theory of allotropy,[1] which postulates the existence in each allotropic modification of an inner equilibrium changing with temperature.

Effect of Different Gases on Rate of Transition.—Although the large majority of the runs were carried out in the presence of air, a few experiments were made with thallous iodide in atmospheres of carbon dioxide or nitrogen. Since the results were the same within experimental error for all three gases, it is concluded that the adsorption of gas by the iodide, if it occurs at all, is a negligible factor in the rate of transition.

Transition Temperatures and Changes of Volume.—While no special effort has been made in this work to determine the exact location of the transition temperatures, the results definitely place them within certain limits. Thus the transformation of mercuric iodide at atmosphere pressure must occur between 123° and 129.5°. Most of the values in the literature are 126° to 127°, but figures as high as 130° have been reported. We have found that the

[1] Smits: "The Theory of Allotropy," (1922).

transition point of thallous iodide lies definitely between 150° and 174° and probably between 160° and 170°. The values recorded in the literature vary from 150° to 190°.

From observation of the total displacement of the mercury level in the manometer when reaction was complete, and from its volumetric calibration (0.028 cc. per cm.), the change of volume accompanying these transitions was obtained, as follows: mercuric iodide, 0.0028 cc. per gram; thallous iodide, 0.003 cc. per gram. These differences in specific volume are exceptionally small. The red form has the greater density in each case.

Summary

A dilatometric method has been developed for measuring the rates of polymorphic transitions of solids in presence of an inert gas. The method eliminates the spurious effects that occur when liquids are used in the dilatometer to transmit the volume changes.

The transitions of mercuric iodide and thallous iodide have been found to be autocatalytic in both directions. The kinetics are similar to those observed in numerous other systems in which one of the reactants and one of the products is a solid phase.

Above the transition point the rates increase very rapidly with increasing temperature. For the change in the reverse direction, the rate at first increases as the temperature is lowered, but then passes through a maximum, and decreases to very small values at liquid air temperature.

The rate is markedly affected by the duration and temperature of heating of the sample previous to conversion.

Approximately equal rates are found in the presence of air, carbon dioxide or nitrogen.

University, Virginia.